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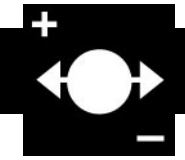
FUSED SALTS: ELECTROPHORESIS



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The interest in this technique is mainly centred around the solution chemistry of molten salts, which had its renaissance in the nuclear field and in the study of nonhydrated ions for the purpose of separating isotopes.

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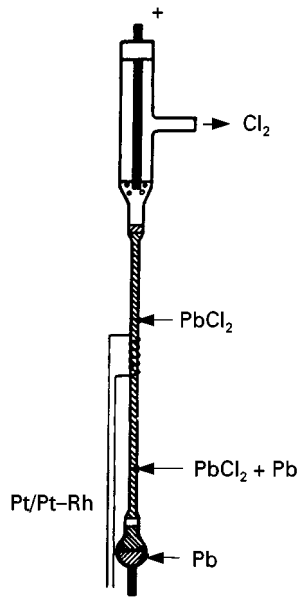

Figure 1 Cell for the determination of mobilities by observation of migrating boundaries. Reproduced with permission from Herzog and Kelmm (1961).

Techniques

Moving Boundary Method

Migrating boundaries can be observed using a cell like that shown in **Figure 1**.

Flat Bed Methods

Electromigration in a support to eliminate convection is carried out much as in normal electrophoresis,

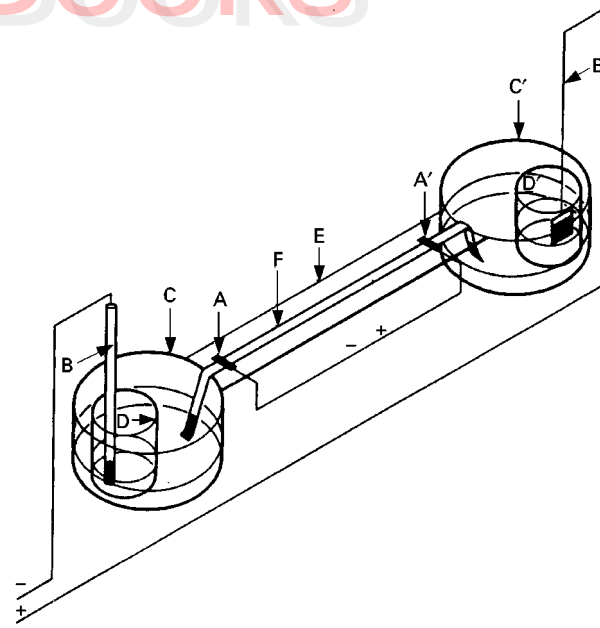

Figure 2 Apparatus for zone electrophoresis in molten salts. A and A′, platinum wires for measurement of potential difference; B and B′, electrodes; C and C′, reservoirs; D and D′, electrode compartments provided with sintered discs at the bottom; E, supporting glass plate; F, electrophoretic strip. Reproduced with permission from Alberti *et al.* (1964).

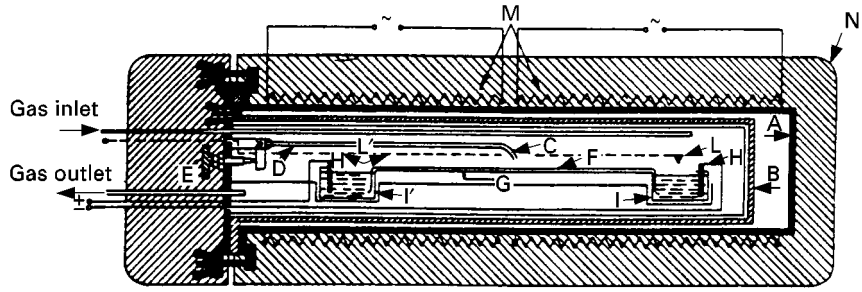

Figure 3 Cross-sectional view of an electrophoretic apparatus. A, furnace; B, electrophoresis chamber; C, capillary; D, tube supporting the capillary; E, screw to raise or lower tube D; F, glass fibre paper; G, heat-resistant glass plate; H and H′, graphite electrodes; I and I′, heat-resistant glass vessels; L and L6, thermocouples; M, Ni–Cr heating wire; N, insulating jacket. Reproduced with permission from Albert *et al.* (1964).

except that here evaporation is negligible and high temperatures are used to keep the molten salt liquid. **Figure 2** shows a typical apparatus. It can be made of glass or fused silica. Glass fibre paper is mainly used as the support material with this apparatus, but it lends itself equally well to electrophoresis on asbestos sheets. This kind of apparatus is best housed in an oven, as shown in **Figure 3**. Here provision is also made to circulate a gas to remove gaseous electrolysis products such as chlorine.

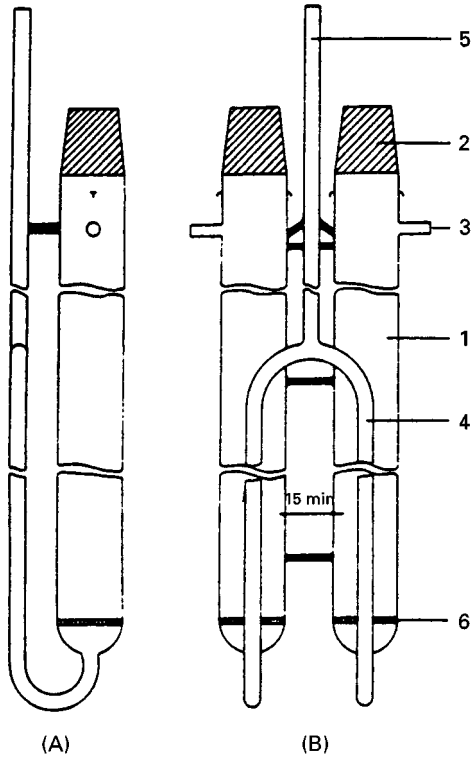

Figure 4 Apparatus for column electrophoresis. (A) Front view; (B) side view. 1, electrode space; 2, ground glass joint; 3 tube for gas evacuation; 4, separation column; 5, tube for admitting the salts to be separated; 6, sintered glass plate. Reproduced with permission from Kühnl and Khan (1966).

Supports

Asbestos paper and asbestos sheets were initially employed as supports; then glass fibre papers became available (e.g. from Whatman). These papers must be washed to removed impurities and are rather

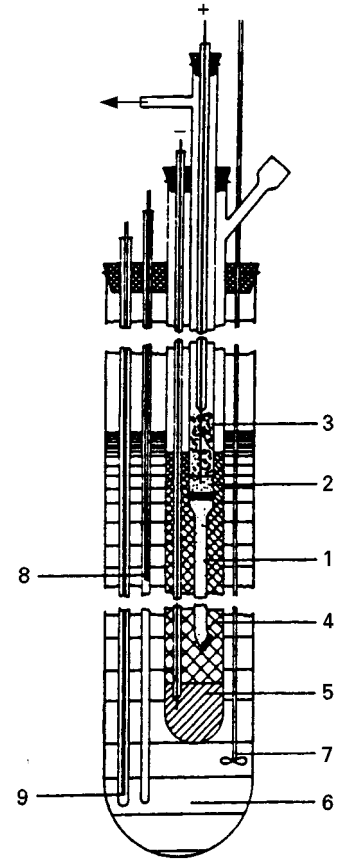

Figure 5 Apparatus for column electrophoresis. 1, separation column; 2, anode compartment; 3, foam at platinum anode; 4, cathode compartment; 5, molten zinc cathode; 6, molten salt bath; 7, stirrer; 8, thermocouple in fixed position; 9, movable thermocouple for measuring vertical temperature distribution. Reproduced with permission from Ljubimov and Lundén (1996).

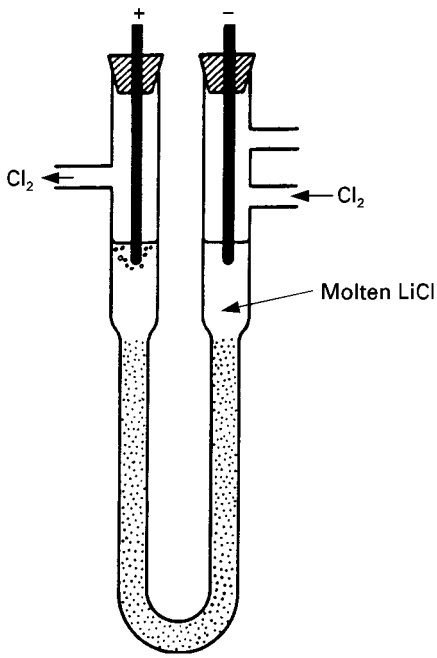

Figure 6 Apparatus used by Klemm for the separation of lithium isotopes. Chlorine is admitted at the cathode to prevent the deposit of metallic lithium. Reproduced from Klemm *et al.* (1947).

fragile, requiring careful handling. Some authors recommend converting the surface silanol groups to salt forms, e.g. by dipping into 4–6 mol L^{-1} KNO_3 at pH 8–9, otherwise the melt does not wet the glass fibre paper.

Powdered thin layers for electrophoresis are made by spraying aqueous suspensions of ceramic oxides onto sintered ceramic strips.

Column electrophoresis is carried out in columns of glass powder, Al_2O_3 splinters, or quartz powder.

Electrodes

Platinum is generally used for the anode, and other materials such as tungsten, nickel, copper or graphite as the cathode. Platinum may be attacked by the alkali metals formed on the cathode during electrophoresis.

Table 1 Effect of mass in electromigration of metals

Isotopes of	*Fused medium*	*Effect of mass*
Li	LiCl	0.14
Li	LiBr	0.26
Li	$LiNO_3$	0.05
Zn	$ZnCl_2$	0.078
Zn	$ZnBr_2$	0.11
K	KNO_3	0.037
Cu	CuCl	0.080
Ag	AgCl	0.064
Cd	$CdCl_2$	0.067
Tl	TlCl	0.040
Pb	$PbCl_2$	0.024

From Chemla (1959).

Table 2 Effect of mass in electromigration of halogens

Isotopes	*Fused medium*	*Effect of mass*
Cl	$ZnCl_2$	0.043
Cl	TlCl	0.086
Cl	$PbCl_2$	0.052
Br	$PbBr_2$	0.042

From Chemla (1959).

Column Electrophoresis

Figures 4 and 5 show two arrangements that can be used for column electrophoresis.

Fused Salts Used as Electrolytes

Numerous electrophoretic mobilities of cations and anions have been published. Most work has been done at relatively low temperatures, i.e. between 150 and 300°C. A lithium nitrate–potassium nitrate eutectic (43 : 57) can be used at 160°C, a sodium nitrate–potassium nitrate eutectic (50 : 50) or lithium chlorate–potassium chlorate eutectic (76 : 24) at 250°C and 300°C, respectively, and potassium nitrate or sodium nitrate at 350°C.

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Isotope Separations

The separation of isotopes performed in aqueous solutions is generally poorer than expected from mass

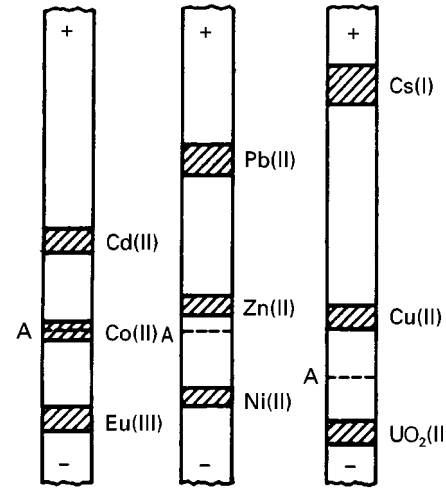

Figure 7 Some representative separations of inorganic ions by zone electrophoresis in molten $LiNO_3$–KNO_3 eutectic–10% NH_4NO_3 at 160°C. A, application point. Reproduced from Alberti *et al.* (1962).

Table 3 Movement of metal ions in fused salts

	Distance moved in 4 h (cm)	*KCl–LiCl eutectic ($T = 450°C$; 2 V cm^{-1})*	*KNO_3–$LiNO_3$ eutectic ($T = 160°C$; 5 V cm^{-1})*
Anionic	0.5–3	Zn(II), Co(II)	
Isoelectric		Th(IV)[a]	Th(IV)[a]
	0.5–3	Ce(III)	Cd(II)
	3–5.5	Pb(II), Cd(II)	Pb(II)
Cationic	5.5–8	Cu(II)	Sr(II), Ba(II), Cs(I), Rb(I)
	8–10.5	Cs(I), Rb(I)	
	10.5–13	Na(I), Ag(I)	

[a]Insoluble precipitate formed. From Alberti *et al.* (1962).

differences, since smaller ions are more hydrated than larger ones and thus mass differences are diminished with fully hydrated ions. This is not the case in molten salts and hence the ionic mobility differences of isotopes are nearer to those expected.

Countercurrent electrophoresis has been used for isotope separation of molten salts. In the system shown in **Figure 6** molten lithium chloride is subjected to electrophoresis and the lithium metal formed on the cathode is reoxidized with a stream of chlorine. At 650°C and a current of 0.5 A, using granular quartz medium to decrease convection, rather high enrichments were reported (from 7.3 to 16.1% ^{6}Li in 4 days). This work served as the basis for a commercial separation of lithium isotopes.

Mass effects depend on the temperature as well as on the anion(s) in the melts. Typical data are shown in **Tables 1** and **2**.

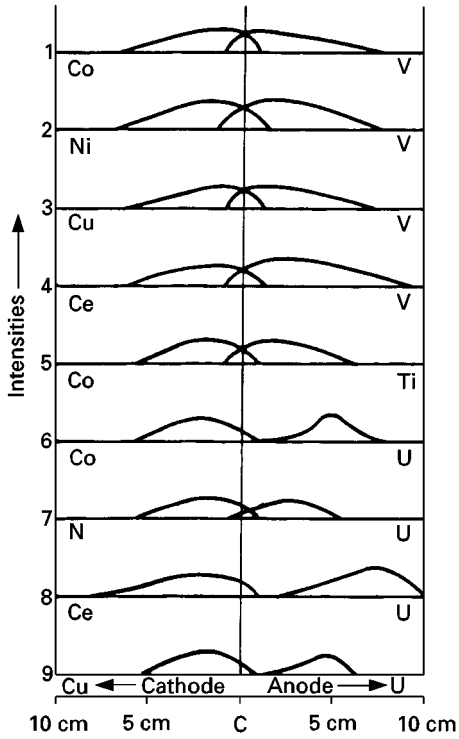

Figure 8 Separations of inorganic ions by column electrophoresis in molten $KHSO_4$–$K_2S_2O_7$ eutectic. Reproduced with permission from Kühnl and Khan (1966).

Analytical Separations of Inorganic Ions

Table 3 gives some data on the movement of metal ions in fused salts and some representative separations by electrophoresis on glass fibre paper are shown in **Figure 7**.

A number of binary metal mixtures have been separated, as shown in **Figure 8**.

The main interest in molten salt separations seems, however, to reside in isotope separations and in the study of ionic mobilities in molten salts. It is worthy of note (see Table 3) that Ag^+ travels as a cation in a KCl-LiCl eutectic, while it readily forms an anionic complex $AgCl_2^-$ in aqueous concentrated HCl solution.

See also: **II/Electrophoresis:** Theory of Electrophoresis. **III/Isotope Separations:** Gas Centrifugation.

Further Reading

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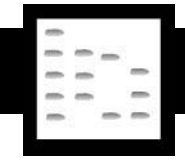
GAS ANALYSIS: GAS CHROMATOGRAPHY



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Introduction

If gases are defined so as to be distinguished from vapours, which is to say only those gases whose critical temperatures are below ambient, and hence cannot be liquefied by pressure at ambient temperature, then the task of gas analysis appears to be a simple one. Applying the criterion of a critical temperature below, say 15°C, produces a very small list of elements and compounds, ranging from helium to ethene. It is, of course, more appropriate to define gases as those which are handled in the gas phase at ambient conditions. Widening the criterion to allow components with boiling points below 15°C produces a rather larger list, ranging from xenon to cyclobutane.

Any gas mixture will be based on one or more of these components, but can in addition contain higher boiling compounds whose low concentration allows them to be present without condensing out from the mixture. As an example, natural gas is treated before it is distributed so that it remains stable in the gas phase over a wide range of temperatures and pressures. It consists predominantly of methane, but contains a large number of other hydrocarbons, up to and including decane, at concentrations which are amenable to direct analysis by gas chromatography.

Analysis for decane and similar components in liquid hydrocarbon mixtures is well established, and similar analytical procedures can be applied to its measurement in natural gas. The main difference is in sample handling and introduction. This will generally be true for other low concentration components of gas mixtures which would normally be liquids or solids. Where techniques exist for analysis of such materials as liquid or solid samples, they can be modified to handle those components in a gas mixture.

This article is not intended to give details of how to analyse all the chlorofluorocarbons or the hydrides of germanium, but aims to show the characteristic differences in equipment and procedures used for gas analysis.

Equipment and Procedures

A chromatograph which is configured for gas analysis will differ in a number of respects from one designed for liquids' analysis. Sample injection will almost invariably be by valve, and other valves may be used to alter the relative positions of different columns during the analysis. Some columns are specifically used for gas analysis, and others may be used in a different way from that for other applications. Carrier gas must be chosen with some care, as it may be a component of the sample, or have properties which do not favour the measurement of sample components. The thermal conductivity detector (TCD) is likely to play a major role; the flame ionization detector (FID) may be regarded as a selective detector in this context.

Sample Handling and Injection

A packed column will handle sample sizes typically in the region of 0.1 to 10 mg. For samples which are liquid, or solids dissolved in a solvent, this means volumes of 0.1 to 10 μL, which are conveniently measured and injected using microsyringes. For gas samples, this mass range approximates to volumes of 0.1 to 10 mL at ambient conditions.

Gas-tight syringes will easily cope with such sample sizes, but the main drawback with using them is poor repeatability, due to injection of a

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